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An apparent failure of the potential gradient concept in electrolysis

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It is a well-accepted principle that a potential gradient exists between two electrodes and none outside whenever a voltage is applied between them Considering figure 1 it is therefore obvious that the electric field is between A (anode) and C (cathode), it is to be noted that the cathode has been placed at a lower level than the anode It is also obvious that there is no field between the surface of the solution (P) and C, this being a region on the outer side of the cathode (to be generally called outer zone or trans-electrodic region We should therefore expect no ionic migration in this overlay region (PC)

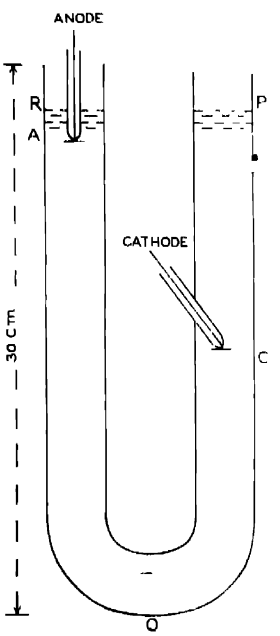

Fig 1

Experimentally, however the ions in the overlay region PC are found to migrate as briskly as in the main body of the solution when a current is passed

between A and C This highly surprising behaviour can be made visually evident if the *U*-tube (figure 1) is filled with say a dilute (N/50 or so) chromic acid solution and a small direct current (say, 5 mA) is passed between the platinum electrodes A and C. It would be found that the coloured anions of chromic acid slowly migrate out of the trans-electrodic zone (PC) until this layer becomes completely colourless As a matter of fact, a fairly sharp boundary can be seen on close examination to have appeared somewhere near C after a short period of electrolysis This boundary C after PC becomes completely colourless migrates slowly towards the anode until it reaches its final limit some-where down in the cathode limb (Palit 1972) between C and Q or slightly above Q on the anode side if the cathode is placed too low Other acids such as H_2SO_4, $HClO_4$, etc behave in the same way though this is not of course visually apparent We have used *U*-tubes up to 5 ft tall and the observation is the same as in our usual 30 cm high tubes. The amount of acid transported out of the zone PC is quite considerable being as high as about one-sixth of the current equivalent passing between A and C The anions thus transported out of the zone PC collect not only in the interelectrode zone AC but some find their way to the region beyond the anode (RA) showing that the induced field (see later) extends to the outer zone of the anode also.

It is to be further noted that the anions move over of the outer zone (PC) not only when an acid solution is used as the electrolyte but also when a neutral salt such as sodium sulphate is used In the latter case the overlay zone (PC) becomes alkaline in preference to the zone CQ after a brief period of electrolysis It is thus evident that anions are moving out of the outer zone (here, PC) where a potential gradient is supposed to be non-existent This counters the idea that diffusion has any role to play in causing such ion depletion. It makes no difference even if a dummy electrode is placed near P and is connected to the cathode to ensure that there is no potential gradient in the zone PC

This kind of exhaustive ion depletion takes place not only from the overlay zone PC but also from a long plastic tube filled with the electrolyte and connected to this overlay zone through the side tube (figure 1) As a matter of fact such *sucking-in* of ions by an electric current takes place from any tube connected to the overlay region Furthermore, a similar behaviour is observed with respect to cations in the transanodic region

Theory

This simple observation is rather surprising and appears almost analogous to the well-known Bernoulli's principle of creation of vacuum near moving fluids. So the essential features can be expressed similarly by saying that an electric current creates *ionic voids* near it and *sucks in* cations and anions along a suitable direction of current flow. There is however an essential dissimilarity with

fluid flow. Here no *sucking-in* has been found to take place from the underlay zone as opposed to the overlay zone, in other words no such ion migration takes place if the two electrodes are in the same tube or in the same limb of a *U*-tube In this connection one recalls that no boundary formation also takes place in a vertical tube (Palit 1972)

The above however is merely a succinct description and explains nothing However, an explanation can be offered on the basis of the well-known fact in static electricity that a free charge inside a medium tends to come out on the outer surface (famous butterfly net experiment in an elementary class) In our experiments the electron cloud which forms on the cathode tends to come out towards P. This creates a potential gradient it the region CP which pushes out the anions As a result of migration of the anions out of CP some alkali would form in the zone CP if sodium sulphate is used as the electrolyte which is in agreement with our observations In general we may think that probably due to the ability of water itself of getting charged both positively and negatively, extra potential gradients get created outside the inter-electrode region and such induced potential gradients are responsible for the observed anomalous migration.

Thus it appears that the potential gradient concept as is well applicable to a gaseous medium or to a solid conductor is not applicable as such to electrolyte solutions The whole thing has more or less the appearance of a cooperative phenomenon where an ion can not be displaced by an electric field without having its effect felt on other ions embedded in the same medium, even if the latter may be far apart and outside the field Further work is in progress and details will be published elsewhere.

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Reference

Palit S. R 1972 *J. Ind. Chem Soc* **49**, 963.